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Fungal Biomineralization of Manganese as a Novel Source of Electrochemical Materials

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Table S1. Comparison of the Energy Storage Capacity of MycMnO_x/C Produced in the Present Study with Other Reported MnO_x Materials Used in Supercapacitors (Related to Figure 4)

Samples	Current Density [A g ⁻¹]	Capacity [F g ⁻¹]	Reference
MycMnO _x /C	1	362	This work
^a Na-OL-1 nanoplates	0.2	308	[S1]
graphene/Mn ₃ O ₄	0.1	271	[S2]
^b MnO ₂ -CNT-G-Ni hybrid	1	251	[S3]
MnO ₂ /reduced graphene oxide	1	242	[S4]
Porous-MnO ₂	0.1	218	[S5]
MnO ₂ /graphene	0.5	210	[S6]
MnO ₂ -modified diatomite	1	206	[S7]
Mn ₃ O ₄ nanoparticles	0.5	205	[S8]
α-MnO ₂	0.3	185	[S9]
3D porous coral-like MnO ₂	1	176	[S10]
^c MG90	0.2	172	[S11]
MnO ₂ -graphene oxide	1	163	[S12]
^d Mn-0.2	0.5	154.5	[S13]
α-MnO ₂	0.25	~150	[S14]
MnO ₂ nanowires	0.5	~125	[S15]
^e λ-MnO ₂ -C	1	120	[S16]
^f MnO ₂ -1h	1	~100	[S17]
^g 3D MnO ₂ -MWCNT	0.2	100	[S18]
α-MnO ₂ -graphene (10 wt %)	1	~90	[S19]

Note: a, Na-birnessite-type MnO₂ nanoplates; b, MnO₂-carbon nanotube-graphene-Ni hybrid foam; c, α-MnO₂/90% (w/v) graphene nanocomposites; d, α-MnO₂ prepared with 0.2 g l⁻¹ sodium dodecyl sulfate addition; e, λ-MnO₂ prepared with concentrated metal nitrates (LiNO₃ and Mn(NO₃)₂·4H₂O); f, MnO₂ was prepared by 1 h hydrothermal reactions; g, 3D MnO₂-functionalized multiwalled carbon nanotube.

Table S2. Comparison of Properties of MycMnO_x/C Produced in this Study with Other Reported MnO_x Materials Used in LiB (Related to Figure 4)

Samples	Capacity/Current density [mA h g ⁻¹]/ [mA g ⁻¹]	Number of cycles	Capacity retention	Reference
MycMnO _x /C	~400/100	200	91%	This work
^a C/MnO-L	600/50	50	>100%	[S20]
hollow porous MnO/C microspheres	755/100	60	92%	[S21]
MnO-attached graphene	650/160	20	90%	[S22]
MnO/carbon nanotubes	~500/188.9	25	90%	[S23]
C/MnO	660/50	50	88%	[S24]
^b MnO@C	563/200	30	~88%	[S25]
MnO/C core/shell nanowires	~500/500	100	~80%	[S26]
MnO ₂ /carbon nanotube	600/200	50	75%	[S27]
α-MnO ₂ hollow urchins	481/270	40	64%	[S28]
δ-MnO ₂	275/40	20	54%	[S29]
MnO	500/100	20	52%	[S30]
MnO ₂ nanowires	~550/200	40	~36%	[S31]
Nanoporous γ-MnO ₂	657/100	20	35%	[S32]
Mn ₂ O ₃	190/200	15	13%	[S33]

Note: a, carbon-containing MnO sample with dark green color; b, MnO coated with carbon layers.

Supplemental Experimental Procedures

Organism and Media

The experimental fungus used was *Neurospora crassa* (FGSC: 2489, Fungal Genetics Stock Centre (FGSC), Kansas, USA). It was routinely maintained on ~25 cm³ malt extract agar (MEA, Lab M limited, Bury, Lancashire, UK) in 90-mm diameter Petri dishes and grown at 25°C in the dark. For liquid culture, *N. crassa* was incubated in a modified AP1 medium consisting of (l⁻¹ Milli-Q water): 20 g D-glucose (Merck, Readington Township, NJ, USA), 20 g urea (Sigma-Aldrich, St. Louis, MO, USA), 1 g MnCl₂·6H₂O (Sigma-Aldrich, USA), 0.9 g K₂HPO₄·3H₂O (Sigma-Aldrich, USA), 0.2 g MgSO₄·7H₂O (Sigma-Aldrich, USA), 0.05 g CaCl₂·6H₂O (Sigma-Aldrich, USA), 0.1 g NaCl (Sigma-Aldrich, USA), 2.5 × 10⁻³ g FeCl₃·6H₂O (Sigma-Aldrich, USA) and trace metals 4 × 10⁻³ g ZnSO₄·7H₂O (VWR, Radnor, PA, USA), and 0.4 × 10⁻³ g CuSO₄·5H₂O (VWR, USA). All the salt and trace element solutions were sterilized separately by autoclaving (121°C, 15 min) and mixed with sterile D-glucose solution when cool. Urea stock solutions (4 M) were sterilized by filtration through a sterile 0.2 µm pore size cellulose acetate membrane filter (Sartorius Stedim Biotech, Göttingen, Germany). The initial pH of AP1 medium was adjusted to pH 5.5 using 1 M HCl after autoclaving. All experiments were conducted at least in triplicate.

Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Analysis (EDXA)

After 12 d incubation, fungal biomass was fixed in 2.5% (v/v_{aq}) glutaraldehyde in 5 mM piperazine-N,N'-bis (2-ethanesulfonic acid) (PIPES) (Sigma-Aldrich, USA) buffer, pH 6.5 (pH was adjusted using 1 M NaOH) overnight at room temperature, and then washed twice using 5 mM PIPES (pH 6.5). Dehydration was performed using a 50-100% (v/v_{aq}) ascending series of ethanol in Milli-Q water (15 min per step) and samples were then dried using a CO₂ critical point dryer (BAL-TEC company, Los Angeles, CA, USA). Samples were mounted using double-sided carbon adhesive tape on aluminium stubs (JEOL, 25 mm × 8 mm) prior to examination by SEM and EDXA. For SEM, samples mounted on stubs were sputter coated for 5 min with gold and platinum (30 nm) using a Cressington 208HR sputter coater (Ted Pella, Inc., Redding, CA, USA). Specimens were examined using a field emission scanning electron microscope (FESEM) (Jeol JSM7400F) operating at an accelerating voltage of 5 kV. For energy dispersive X-ray analysis (EDXA) (Oxford Inca, Abingdon, Oxon, UK), uncoated samples were used, and operation was at an accelerating voltage of 15 kV for at least 100 s.

X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) of Fungal Biominerals

The mineralogy of the sample was determined using a Hiltonbrooks X-ray diffractometer (Hiltonbrooks Ltd., Crewe, UK) fitted with a monochromatic CuK α source and curved graphite, single crystal chrometer (30 mA, 40 kV). The sample was ground to a powder using a ceramic mortar and pestle and then firmly compacted on the reverse side of an aluminium specimen holder (15 × 20 × 2 mm³) held against a glass side. After compaction, the back cover was snapped into place and the glass side removed from the holder. Duplicate samples were analysed over the range 3-60° 2 θ at a scan rate of one degree/min in 0.1 degree increments.

For FTIR, the test sample, standard Mn₃(PO₄)₂ and KBr were dried in an oven at 105°C overnight. The test sample was mixed with KBr (v:v = 1:100) and continuously ground to a fine powder for about 6 min using an agate mortar and pestle. The sample was transferred to a 13 mm Evacuatable Pellet Die and pressed into a transparent pellet using a 15 Ton Manual Hydraulic Press (Specac Ltd., Orpington, Kent, UK). FTIR spectra were recorded over the region 4000-400 cm⁻¹ using a PerkinElmer Spectrum GX FTIR system (PerkinElmer Instruments, Waltham, MA, USA) purged with CO₂-free dry air. A KBr pellet was used as a background control.

XPS data were collected on a Scienta ESCA-300 instrument (Scienta AB, Uppsala, Sweden) fitted with a conventional non-monochromatic Al-K α X-ray source and a multichannel video detector. The binding energies were referenced to the Ag 3d_{5/2} peak at 368.4 eV. XPS spectra were analyzed using the computer-aided surface analysis for XPS (CasaXPS) software (Casa Software Ltd, Teignmouth, Devon, UK) and a 30% Gaussian-Lorentzian function was used for the curve fitting procedure.

Electrochemical Measurements

To prepare activated carbon (AC), petroleum coke (~ 200 mesh) was mixed with KOH (w:w = 1:4) and ground to a fine powder using a ceramic mortar and pestle prior to being loaded into a stainless steel vertical tube. Carbonization of the precursor was achieved by increasing the temperature to 765°C at a heating rate of 5°C min⁻¹, which was then

maintained for 1h. Argon gas was used to purge the atmosphere during carbonization process. When cooled down to room temperature, the sample was washed several times with distilled water (with the pH adjusted to neutrality using 1 M HCl) and then dried in a vacuum furnace at 75°C for 12h.

To prepare mycogenic MnO_x/C, fungal biomass was collected after 12 days incubation by centrifugation (4770 g × 20 min, 4 °C), dried in a desiccator for several days, and then heat treated at 300°C for 4 h. For the supercapacitor, the working electrode was prepared by evenly mixing mycogenic MnO_x/C (MycMnO_x/C), acetylene black (AB) and polytetrafluoroethylene (PTFE) (*w:w:w* = 70:20:10) which was continuously ground to a paste, and then coated onto a nickel foam substrate to form a 1.6 mm diameter electrode sheet. The counter electrode was prepared using the same method, with the activated carbon (AC), AB and PTFE being mixed (*w:w:w* = 85:10:5) to form a paste and being coated onto the nickel foam substrate. Electrochemical measurements of the supercapacitor were conducted using a two-electrode system (asymmetrical hybrid supercapacitor) comprising a MycMnO_x/C working electrode, an AC counter electrode and a 1 M Na₂SO₄/5.4 M KOH aqueous solution as the electrolyte. Cyclic voltammetry (CV) measurements were carried out using a CHI660E workstation (Chenhua, Shanghai, China) and the galvanostatic charge/discharge measurements were obtained using a Neware CT-4008-5V50mA tester (Neware, Shenzhen, China).

The electrochemical measurements of lithium-ion batteries were carried out using coin-type CR2025 cells, and the working electrode was prepared by mixing MycMnO_x/C, AB, and PTFE (*w:w:w* = 75:20:5) in 100% ethanol, which was then rolled into sheets and punched to provide ~1.4 cm diameter electrodes. The electrodes had a mass loading of 2 ~ 3 mg cm⁻¹ after drying at 75°C overnight under vacuum, and then were pressed onto the nickel foam. The electrolyte used was 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (*v:v* = 1:1). Pure lithium foil was used as the counter electrode, and the separator was a polypropylene membrane (Celgard, Charlotte, North Carolina, USA). Cyclic voltammetry (CV) measurements and galvanostatic charge/discharge tests were carried out as described above.

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